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BY

WALLACE REED BRODE

B.S. Whitman College, 1921
M.S. University of Illinois, 1922

V.C.

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1925

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[Contribution from the Chemical Laboratory of the University of Illinois]

OPTICALLY ACTIVE DYES
II. ADSORPTION, ABSORPTION SPECTRA AND ROTATION

By Wallace R. Brode[1] with Roger Adams

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In a previous article by Ingersoll with Adams[2] a very convenient method was described for the preparation of pairs of enantiomorphic dyes. The research had as its ultimate object the determination of whether the mechanism of dyeing of fibers was a physical process, a chemical process, or both. With the pure *d* and *l* forms of a dye, a comparison of the two equivalent solutions as regards adsorption by the fiber could be made. By means of a colorimeter or, perhaps, polarimeter, the concentration of the partially exhausted *d* and *l* solutions could be compared with each other and with the original solutions. The assumption was that compounds that are mirror images would have the same dyeing properties provided the adsorption by the fiber was a purely physical process. On the other hand, if a chemical reaction of any sort took place when the dye was adsorbed, the degrees or rates of adsorption of the *d* and *l* forms might be different on account of the optical activity of the substance of which the fiber was composed.

In order to be sure that, if such results as have been mentioned were

[1] This communication is an abstract of a portion of a thesis submitted by Wallace R. Brode in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Ingersoll with Adams, This Journal, **44**, 2930 (1922).

obtained, it would be proper to draw the above conclusions, certain assumptions are necessary. First, the physical adsorption of the *d* and *l* forms would be equal under like conditions. Second, the absorption spectra of the *d* and *l* forms are the same, otherwise it would be impossible by means of a colorimeter to determine the amount of dye adsorbed from the solution of the two dyes. Third, the change in the hydrogen-ion concentration as a result of the addition of an adsorption medium to the dye solution would not affect the rate of adsorption by the fiber or the color of the solution within experimental error. If an appreciable change in the hydrogen-ion value of the solution took place during treatment of the solution by the fiber, it would complicate the quantitative determination of the amount of dye in solution and necessitate the control of the hydrogen-ion concentration in the solution when the polarimeter and colorimeter readings were made.

Before preparing a number of pairs of optically active dyes and studying their adsorption by fibers, it seemed advisable to study one pair and determine whether experiment would substantiate these assumptions and warrant a detailed study of the mechanism of dyeing by the general method planned. In this communication the β-naphthol derivatives of the diazotized *d*, *l* and *dl*-phenyl(*p*-aminobenzoylamino)acetic acid, $HO_2C—CH(C_6H_5)NHCOC_6H_4N{=}NC_{10}H_6OH$, were chosen for study, since this set of dyes is easily prepared and purified. The work was divided into four parts: (1) the adsorption of these dyes by various inactive physical adsorbing reagents; (2) the determination of the absorption spectra; (3) the effect of hydrogen-ion concentration upon the absorption spectra; and (4) the determination of the optical rotation of these dyes.

Adsorption

The adsorption of a dye by charcoal or an inorganic adsorbing medium has been conceded by many[3] to be of a physical nature although the point has not been generally decided. If such adsorption were chemical, the fact that the charcoal adsorbs equal amounts of the *d* and *l* does not conflict with the deduction that the action of the fiber in adsorbing different amounts of the *d* and *l* dyes is chemical. Equal adsorption by charcoal and inorganic adsorbing agents even if chemical in nature, would be a question of adsorption by a symmetrical substance, whereas fibers are unsymmetrical substances.

A number of different adsorbing media were tested, including Tennessee ball clay, kaolin, silica, alumina, aluminum hydroxide, Sil-O-Cel, fuller's

[3] Wood, "Chemistry of Dyeing," D. Van Nostrand Co., **1913.** Dreaper, *Trans. Faraday Soc.*, **6,** 31 (1910). W. C. McC. Lewis, *Phil. Mag.*, **15,** 499 (1908). Liddell, "Chemical Engineering Handbook," McGraw-Hill Book Co., **1923,** Vol. II, p. 780 (Jerome Alexander). Gee and Harrison, *Trans. Faraday Soc.*, **6,** 42 (1910). Freundlich, *Z. physik. Chem.*, **57,** 385 (1906); **59,** 204 (1907).

earth and charcoal. Silica and alumina adsorbed the dyes only slightly, not enough to give good results. Sil-O-Cel and fuller's earth adsorbed satisfactorily, but difficulty was experienced in the centrifuging of the material. The adsorption by Tennessee ball clay, charcoal and kaolin was not complicated by these difficulties and gave satisfactory results, the first two of these adsorbing agents being used for the adsorption experiments.

For the absorption experiments, the *d*, *l* and *dl* forms of the dye were dissolved in molecular equivalents of alkali solution; the hydrogen-ion concentrations of these solutions were determined, to be certain that they were the same. Although a change in hydrogen-ion concentration of the solutions by the addition of acid or alkali was claimed by Abderhalden[4] to have no effect on the adsorbing power of charcoal, the solutions of the dyes in this investigation were prepared with the same hydrogen-ion concentration to remove any possibility of change of color or solubility which would thus affect the quantitative determination with a colorimeter of the amount of dye adsorbed.

Adsorption by Tennessee Ball Clay.[5]—Dilute solutions of the *d*, *l* and *dl* dyes, each containing 0.01428 g. of the dye in 50 cc. of water containing a molecular amount of alkali, were well shaken with 0.0304 g. of clay. The mixtures were allowed to stand for three weeks in tightly corked containers; then the clear supernatant liquids were pipetted off and centrifuged for half an hour to remove any fine suspended particles. The original solutions and the exhausted solutions were then compared in a Duboscq colorimeter in all possible combinations. The actual difference in any solutions before and after treatment could be determined indirectly through fifteen sets of readings, thus giving a very close check on the readings obtained. The errors in the readings were much less when solutions of approximately the same concentration were compared, such as the original *d* and the original *l*, or the exhausted *d* with exhausted *l*. There was considerably more variance when the original *d*, *l* or *dl* was compared with the exhausted *d*, *l* or *dl*. The color intensity of these solutions was a measure of the quantity of dye present.

Adsorption by Charcoal and by a Mixture of Charcoal with Silica.—Since preliminary experiments showed that the amount of dye adsorbed by powdered silica was negligible, the presence of this material did not affect the adsorption value of the charcoal, but merely diluted the dye and made possible more accurate determination of the amount of charcoal used. The ordinary animal charcoal was employed. The mixture

[4] Abderhalden and Foder, *Fermentforschung*, **2**, 74 (1917).

[5] Clay used for this experiment was obtained from the Ceramics Department of the University of Illinois. It gave an approximate analysis of silicon dioxide, 47%; aluminum oxide, 38%; titanium oxide, 1%; iron oxide, 1%; calcium and other oxides 0.5%; moisture, 12%; organic matter, 0.5%; 98% of this clay passed through a 200-mesh sieve.

with silica consisted of 1 g. of silica with 0.1 g. of charcoal. From this mixture weighed portions were used for each experiment. In each case, the weighed amount of adsorbing agent was added to the solutions which were then thoroughly shaken and allowed to stand at room temperature for a period of five hours in the case of pure charcoal and ten hours in the case of the silica-charcoal mixture. The liquid was then pipetted off and centrifuged for one hour at high speed. The amount of dye in the clear, supernatant liquid was then determined as previously described under the experiments with Tennessee ball clay.

Determination of the Colloidal Nature of the Dye.—Fifty cc. each of the *d*, *l* and *dl* solutions as used in the adsorption experiments was filtered through a collodion filter such as is used in ultrafiltration. Filter paper of a quantitative grade was soaked in a 3–4% collodion solution in glacial acetic acid and then immersed in water and kept under water until used. The dye solutions were filtered under an air pressure of about four atmospheres and the percentage of color change in the two solutions was determined by a colorimeter as in the preceding experiments. The amount of dye not retained by the membrane was thus determined. The experiments showed that more of the *dl* form existed in a colloidal state than of the *d* or *l* solutions, a fact which would be expected from their solubility.

TABLE I

ADSORPTION OF DYES

	Tennessee ball clay		Charcoal		Charcoal and silica		Contained colloids	
	0.0304 g. used 0.01428 g. of dye 50 cc. of soln. P_H 8.4		0.0200 g. used 0.00625 g. of dye 25 cc. of soln. P_H 7.2		0.0150 g. used 0.00625 g. of dye 25 cc. of soln. P_H 7.2		Colloids 0.0125 g. of dye 50 cc. of soln.	
	Adsorbed %	Error ±	Adsorbed %	Error ±	Adsorbed %	Error ±	Colloids %	Error[6] ±
d	35.9	0.59	41.96	0.45	19.05	0.61	73.50	0.29
l	35.8	.94	41.93	.27	19.09	.61	74.66	.14
dl	41.7	.48	46.25	.22	27.05	.49	84.71	.12

Results

The above results bring out two very important points. In the first place, they show that the active forms are adsorbed to the same extent in the case of inactive adsorbing media where there is no possibility for a true chemical action. This does not mean, however, that the adsorption by these media is necessarily physical in character, since equal adsorption might be expected in the case of chemical combination with a symmetrical adsorbing agent. The conclusion can be drawn that if any difference in the adsorption of the dyes by symmetrical and asymmetrical adsorption agents could be detected, it would be due to chemical reaction.

In the second place, there is shown the necessity of having absolutely pure dyes with which to carry out these experiments, as the racemic form has a higher adsorption. This would naturally be expected from the fact

[6] The probable error in this experiment and with others following was calculated from the formula $\frac{0.8453\,\Sigma\,(+v)}{n\sqrt{n-1}}$ in which $\Sigma\,(+v)$ is the sum of the deviations of all individuals from the mean, without regard to the sign and n is the number of individuals. Mellor, *Means and Average Errors* in "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co., 1913, pp. 524–531.

that it has a much lower solubility and a higher percentage in a colloidal state, than the active forms do. The presence of any racemic form in one of the active dyes would interfere seriously with adsorption experiments with fibers.

Absorption Spectra

If the enantiomorphic forms did not have the same absorption spectra, it would be impossible to make accurate quantitative determinations of the amount of dye in the solutions by means of a colorimeter. The identity of the absorption spectra of various stereo-isomers has been investigated by a number of writers[7] and the general results conform with the rule given by Kayser[8] that "substances with similarly related structure give similar molecular vibration curves, whereas substances with different structures give different curves. This applies without exception to aromatic compounds as well as to alkaloids, dyes and colored substances." The results obtained in this paper agree with this general rule and with the facts obtained by various other workers, that the optical enantiomorphs show the same frequency of vibration. The previous work, however, as a rule has included only two of the possible three forms, usually the *d* and *dl* as with corydaline;[7a] or else compounds were used in which the color ion was separate from the group containing the asymmetric carbon atom as in the case of copper tartrate.[7c,7d] The effects of color and rotation in compounds such as the latter are not necessarily connected.

The solutions of the *d*, *l* and *dl* β-naphthol dyes for the determination of the absorption spectra in the visible contained 0.01 g. of dye per 1000 cc. and in the ultraviolet contained 0.025 g. per 1000 cc. Whenever the three dye solutions were compared, care was taken that the hydrogen-ion concentration in each of the three was the same. The solutions used had a Sörensen value (*P*H) of 7.8.

The method for plotting the curves showing the transmission for different wave lengths was similar to that used by the Bureau of Standards[9] in which $-\log_{10}$ of the transmittancy was plotted against the wave length or frequency, depending upon whether the measurements were in the visible or in the ultraviolet. The extinction coefficient in this case was k, where $k = \frac{1}{bc}(-\log T)$, in which b is the length of the tube, c is the con-

[7] (a) Dobbie and Lauder, *J. Chem. Soc.*, **83**, 605 (1903). (b) Gadamer, *Arch. Pharm.*, **239**, 648 (1901). (c) Stewart, "Stereochemistry," Longmans, Green and Co., **1919**, p. 34; *J. Chem. Soc.*, **91**, 199, 1537 (1907). (d) Cotton, *Compt. rend.*, **120**, 989, 1044 (1895). (e) Hartley and Huntington, *Proc. Roy. Soc.*, **31**, 1 (1881). (f) Magini, *J. chim. phys.*, **2**, 407 (1904).

[8] Kayser, "Handbuch der Spectroscopie," Hirzel, Leipzig, **1905**, Vol. III, p. 213.

[9] "Spectral Transmission of Dyes," Gibson and others, *Bur. Standards Bull.*, **440**, Vol. 18, p. 128 (1922).

centration, T the transmittancy which equals I/I' where I and I' represent the intensity of light entering and leaving the cell.

The absorption spectra in the ultraviolet was determined at the Bureau of Standards on a Hilger sector photometer.[10] The apparatus used is described in detail in Bull. 440 of the Bureau of Standards.[9] Photographic exposures were made at various transmittancies and from these plates the curve was determined. The absorption bands in the visible were determined in part by the Koenig-Martens spectrophotometer at the Bureau of Standards,[9,11] and in part by the Keuffel and Esser spectrophotometer at the University of Illinois. The Koenig-Martens instrument employs a Wollaston prism as a polarizer and uses Nicol prisms to measure the

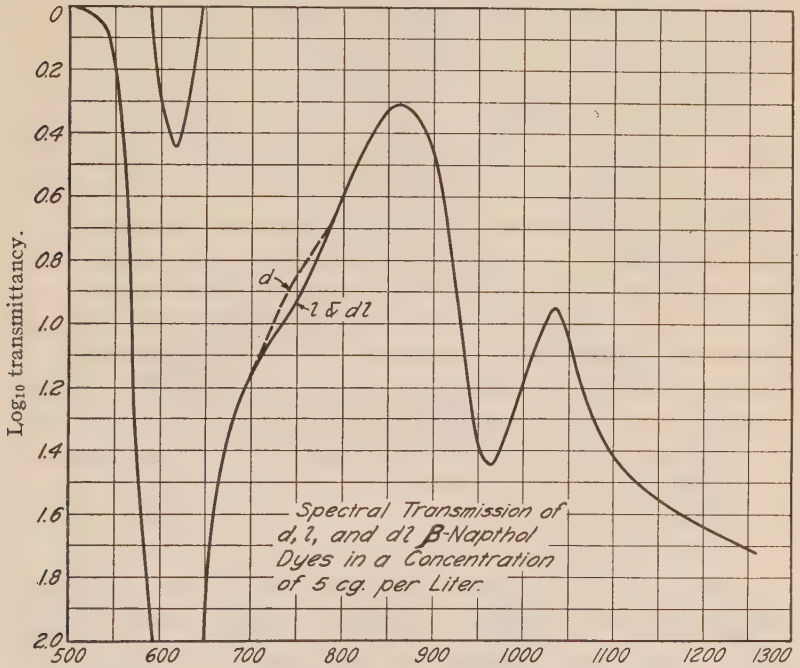


Fig. 1.

intensity of the polarized light coming through the sample and the solvent. The Keuffel and Esser spectrophotometer employs sector disks as a means of controlling the light passing through the solution containing the dye.

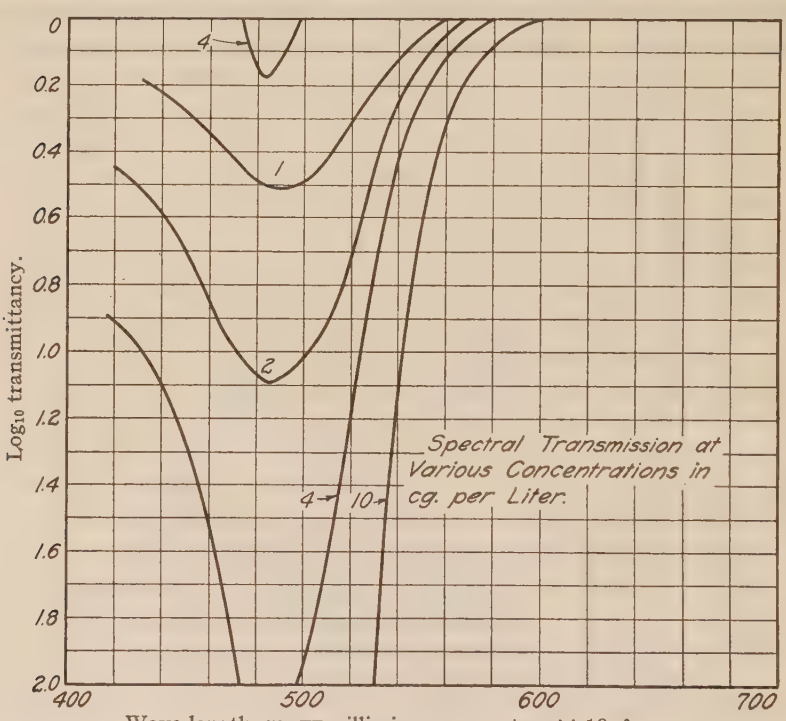
All three dyes gave bands of the same frequency both in the visible and the ultraviolet. In the case of the *d* dye a small difference was observed

[10] The authors are indebted to the colorimetric section of the Bureau of Standards for help and suggestions in carrying out these determinations.

[11] *Ann. Physik* [4] **12,** 985 (1903).

in the height of one of the bands, which is indicated by a dotted line on the graph (Fig. 1). This difference was so small that it did not affect the shade of the color sufficiently to be detected in the Duboscq colorimeter since this colorimeter does not employ spectroscopic dispersion by the use of monochromatic light of wave length of the maximum absorption as the means of determining the color intensity. It is not out of the question that a slight impurity was the cause of this difference in one of the bands.

The band in the visible was of a wave length of 486 mμ or a frequency of 625. The bands in the ultraviolet appeared at frequencies of 788, 956

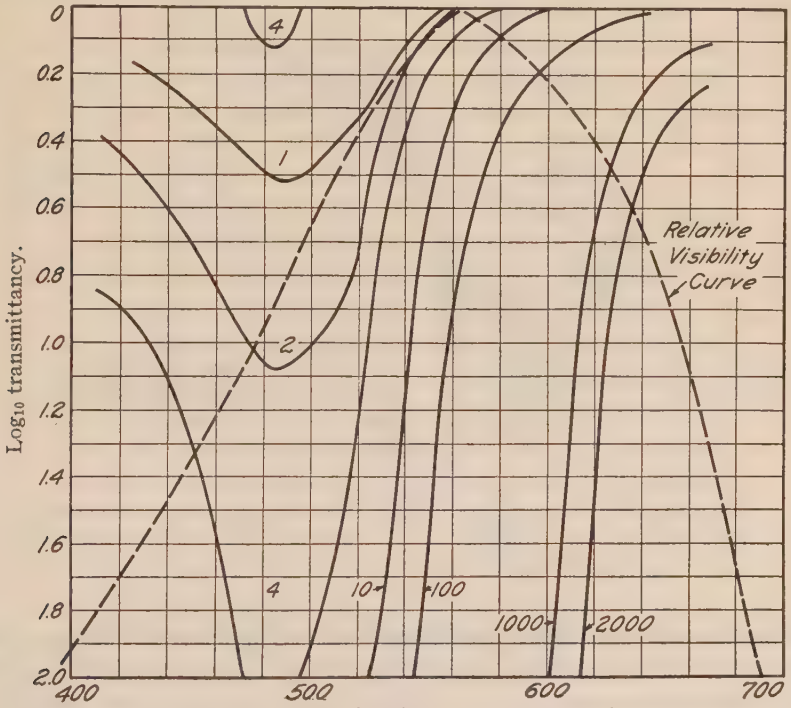


Wave length, mμ ≡ millimicrons ≡ meters × 10^{-9}.

Fig. 2.

and 1108. These bands are approximate multiples of the definite fundamental frequency of 158, the first band in the spectrum corresponding to the fourth period and the others to the fifth, sixth and seventh periods. The light transmission of these dilute solutions of the dyes were shown to vary in accordance with Beer's law, the logarithm of the transmission being directly proportional to the concentration (Fig. 2) and the thickness (Fig. 3). In determining the transmission of various concentrations, solutions of 1, 2, 4, 10, 100 and 1000 cg. per liter were used. Transmission at various thicknesses of the solutions was determined by using tubes of 1, 2, 4, 7 and 10 cm. in length.

If the optical isomers, especially the two active forms, had not had the same frequency of absorption, the comparison of the two by means of a colorimeter would have been impossible; a difference in the intensity of the two bands would also complicate the determination of the dyes in the solutions by the colorimetric method. As has been shown in these results, however, the three enantiomorphic forms had bands of the same intensity throughout the visible spectrum. In a quantitative determination of the absorption of the dye by adsorbing media, the validity of Beer's law was assumed. This law was shown to hold for the solutions of the strength used in these experiments.



Wave length, mμ ≡ millimicrons ≡ meters × 10^{-9}.

Fig. 3.—Visible spectra transmission at various thicknesses in cm.

The Effect of Change in Hydrogen-Ion Concentration upon the Absorption Spectra

The addition of an adsorbing agent to a solution almost invariably changes the hydrogen-ion concentration of the solution, the character of the change depending upon whether the adsorbing medium is of a negative or positive character.[12] It was, therefore, essential to determine the color change which is effected by the change in hydrogen-ion concentra-

[12] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 155.

tion. The strength of the solutions used for this experiment was the same as those used in the determination of the absorption spectra in the visible. The hydrogen-ion concentration of the solution was determined electrolytically. The change in color with the change in hydrogen-ion concentration in the case of the β-naphthol dyes is very slight between P_H 3 and 8.5, but beyond 8.5 a sharp drop in the band takes place and secondary bands appear at 443 and 516 mμ (Fig. 4). A similar effect is shown when the solution is made strongly acid. At P_H 1.2 there is a sharp change with the appearance of two bands at 522 and 553 mμ (Fig. 5). This curve does not change in shape but simply drops in height, due possibly to the formation of larger colloidal particles.

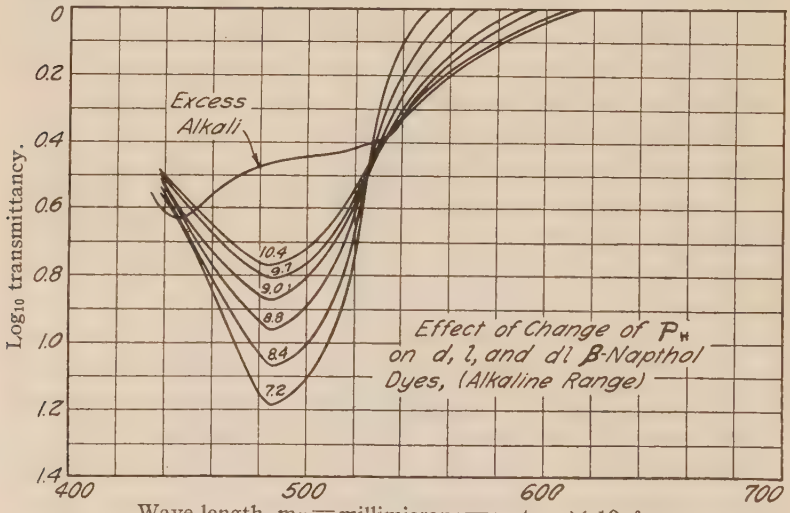


Fig. 4.

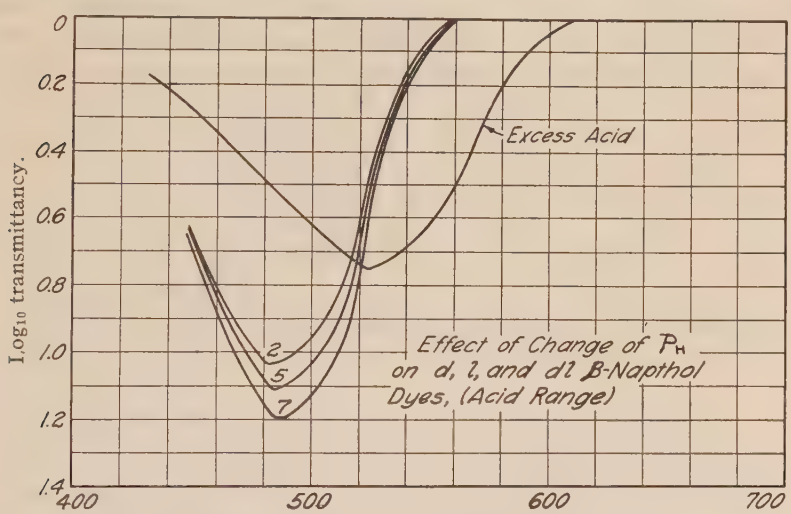
It has been shown in the experiments described above that the absorption band does not change in wave length but rather in intensity with a change in hydrogen-ion concentration. This does not lead to the conclusions of Smith and Boord,[13] that the band shifts with an increasing alkalinity. The change in intensity without change in wave length has been applied to the study of indicators. A method has been developed by which hydrogen-ion concentration could be determined by taking this fact into account.[14]

From the results obtained, it is seen that the band reaches approximately its maximum height at P_H 7 to 8 and a change of 1 or 2 in the Sörensen value on either side does not change the color intensity of the solutions sufficiently to be detected by a colorimeter of the type used in this in-

[13] Smith and Boord, THIS JOURNAL, **44**, 1449 (1922).

[14] Brode, *ibid.*, **46**, 581 (1924).

vestigation. The hydrogen-ion concentration in all these experiments did not vary within the experimental error and did not complicate the data in this research. The solutions used in the adsorption experiments had a Sörensen value of 7 to 8 and the actual hydrogen-ion change, after treatment, did not exceed 0.5 P_H. It was permissible, therefore, to assume that the color change due to the change in hydrogen-ion concentration by adsorption was negligible.



Wave length, mμ ≡ millimicrons ≡ meters × 10^{-9}.

Fig. 5.

Rotation

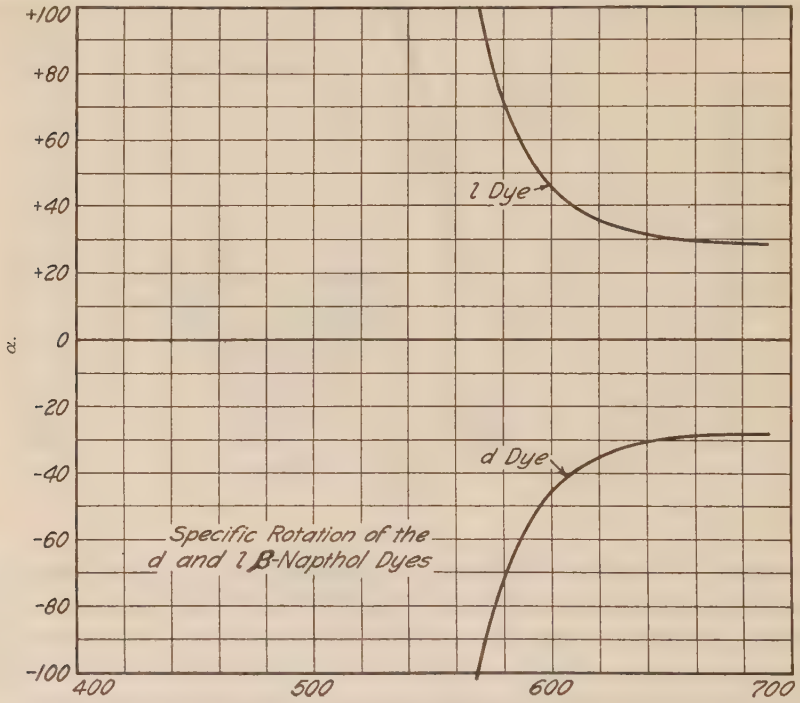
Rotation of colored substances at different wave lengths presents a characteristic curve due to the proximity of the absorption band. This relation between the rotation and absorption bands has been studied by Lowry, Akermann, Drude, and others,[15] and the curves presented in this paper are of the same type as those obtained by previous workers.

The rotation of these dyes was very difficult to obtain, due to their physical properties, several of the difficulties being almost impossible to overcome. The dyes being red, monochromatic light sources such as sodium and mercury were eliminated for the determination of the rotations. Previous workers have described apparatus for the determination of rotations at various wave lengths other than those furnished by monochromatic light sources.[16] The best results for these dyes were

[15] Lowry, *Trans. Faraday Soc.*, **10,** 106 (1914); *J. Chem. Soc.*, **107,** 1196 (1915). Lowry and Austin, *Trans. Roy. Soc.* (London), **222A,** 272 (1922). Pickard, *J. Chem. Soc.*, **123,** 435 (1923). Akermann, *Ann.*, **420,** 1 (1920).

[16] *Bur. Standards Bull.*, **44,** 17 (1918). Bates, *Astrophys. J.*, **8,** 214 (1898); *Phil. Mag.*, **18,** 320 (1909). Patterson, *J. Chem. Soc.*, **109,** 1143 (1916).

obtained by the use of a 7-ampere, 20-volt straight condensed filament lamp. The filament was about 16 mm. long and, on overloading, gave about 200 candle power. The filament image was projected on the slit of a spectroscope and by making both the entrance and exit slits as narrow as possible, nearly homogeneous light of a mono-chromatic nature was obtained. The spectroscope used was one attached to a polarimeter which was a large Franz Schmidt and Haensch instrument capable of reading to 0.0002°. Due to the construction of the spectroscope, however, as the far red end of the spectrum was approached, the dispersion



Wave length, mμ ≡ millimicrons ≡ meters × 10^{-9}.

Fig. 6.

became less so that the readings obtained beyond a wave length of 650 mμ are of no great quantitative value. The rotation of the *d* dye (that is, the one obtained by diazotization and coupling of *d*-phenylamino-benzoyl-amino-acetic acid) in this case was negative and that of the *l* dye was positive (Fig. 6). These dyes act similarly to amino acids in that on long standing with sodium hydroxide, racemization takes place, and in the case of saturated solutions of the active forms the *dl*, which is less soluble, precipitates. The probable reason for the failure to obtain rotations of the dimethylaniline dye in sunlight[17] was that the rotation of the dye approached zero

[17] Ingersoll with Adams, This Journal, **44**, 2930 (1922).

at the wave length where the absorption curve crossed the maximum sensitivity curve of the eye. At other wave lengths, however, rotations could be observed, the rotation being positive on one side and negative on the other. The rotations by sunlight involve various wave lengths and since the rotation is dependent on the wave length, the results obtained by sunlight, or any heterogeneous source which is not treated so as to obtain a light of monochromatic nature, are of no great quantitative value.

Summary

1. The adsorption of enantiomorphic forms of dyes by charcoal, clay and other inactive adsorbing agents is the same.

2. The adsorption of the racemic form of these optically active dyes is different from that of the active.

3. The active forms exist more nearly in the form of true solutions than does the racemic modification.

4. The absorption spectra of the optical enantiomorphs give bands of the same frequency.

5. The change in hydrogen-ion concentration of the dye solutions does not change the wave length of the band but rather the intensity of the various bands.

6. Within the range of hydrogen-ion concentration change involved in the use of common adsorbing agents, the change of color of these particular dyes is negligible and the possible difference in the intensity of the two forms is negligible as far as the use of colorimetric determinations is concerned.

7. Beer's law is applicable to the dilute solutions used in these experiments.

8. As far as studied, the rotation of these dyes and intermediates is normal.

From these statements it is apparent that these dyes are suitable for future experiments in connection with the possible mechanism in the dyeing of wool and other fibers containing active constituents.

URBANA, ILLINOIS

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[Contribution from the Chemical Laboratory of the University of Illinois]

THE DETERMINATION OF HYDROGEN-ION CONCENTRATION BY A SPECTROPHOTOMETRIC METHOD AND THE ABSORPTION SPECTRA OF CERTAIN INDICATORS[1]

By Wallace R. Brode

Received November 23, 1923

In the study of the absorption spectra of dyes and other colored organic substances in aqueous solutions, knowledge of the hydrogen-ion concentration of the solutions is quite essential, due to the variation of the absorption band in shape and intensity with various hydrogen-ion concentrations. Several methods have been suggested for the colorimetric determination of hydrogen-ion concentration of colored solutions, but all of them are more or less complicated and in most cases give only approximate results.[2]

All of these methods require the use of a colorimeter or other special apparatus, whereas the suggested spectrophotometric method employs no apparatus in addition to that necessary for the determination of the absorption band of the colored solution, and may be made in a comparatively short time after the completion of the determination of the absorption band.

It was observed in the spectrophotometric study of certain dyes at various hydrogen-ion concentrations,[3] that on the change of the hydrogen-ion concentration of the dye solution the absorption band did not shift gradually in wave length but merely changed in height. In the same manner the absorption bands of the indicators studied did not shift in wave length with a change in hydrogen-ion concentration but varied in intensity while, in most of the cases observed, another band proceeded in the opposite direction at the same time. By using the same concen-

[1] This paper is the result of suggestions derived from a paper given by Buswell and Smith on "Color Standards in Water Analysis," at the 1923 Spring Meeting of the American Chemical Society, in which the absorption spectra curves of phenol red for various hydrogen-ion concentrations were determined in a manner somewhat similar to the method used in this paper, and a paper by Baker and Davidson (see Ref. 4d) on "Spectroscopic Measurements of the Hydrogen-ion Concentration Color Changes in Recent Indicators."

[2] (a) Gillespie, *J. Bact.*, **6**, 399 (1921). (b) Meyers, *J. Biol. Chem.*, **50** [Proc.] 22 (1922). (c) Everz, *Analyst*, **46**, 393 (1921). Other references as given in (d) Clark's "The Determination of Hydrogen Ions," Williams and Wilkins Co., **1922**, pp. 66–73.

[3] Brode with Adams, Forthcoming article in This Journal, **46** (1924).

tration of indicator in all solutions the hydrogen-ion concentration of an unknown solution may be determined by comparing the height of its absorption band with those obtained from solutions of known hydrogen-ion concentrations. Any absorption due to the color of the original solution may be counteracted and its effect removed by using the original solution in the comparison cell. Since the height of the band varies, within certain ranges, with the hydrogen-ion concentration of the solution, it is necessary only to use a standard quantity of indicator solution to give a colored solution, the height of whose absorption band may be compared against the standard curves presented in this paper and the hydrogen-ion concentration determined.

The method proposed is not new or distinctive but very few data has been prepared on it and a large part of these data have been determined with a simple spectroscope, rather than by using a spectrophotometer, so that only the edge and not the peak of the band was determined.[4] A study of the series of curves presented in this paper will show that such a treatment does not lead to accurate or conclusive results in regard to the effect of hydrogen-ion concentration on the absorption spectra of these various indicators. Baker and Davidson have determined the absorption spectra of a number of the Clark and Lubs indicators at various Sörensen (P_H) values, the curves being determined photographically and not photometrically. Their data, although not of the same degree of accuracy as attainable by a spectrophotometric method, confirm the fact that the band changes in intensity but not in frequency with a gradual change of the Sörensen value. The object of their work was to devise a new method to determine Sörensen values by spectrophotometric means. The determination of the dissociation constant of phenolphthalein by means of the change in height of the absorption band of that indicator[5] presents a method of determination which is quite similar to the proposed method for the determination of hydrogen-ion concentration. The measurement of the change in the amount of color content of one particular type in certain indicators with a change in P_H is an approach at the same type of measurements as carried out in this paper.[6]

A number of indicators were tried so as to ascertain the best for the determination of certain hydrogen-ion concentrations and to obtain a range of curves that would cover a hydrogen-ion concentration of 1 to 10 P_H, inclusive. The most suitable type of indicator for this purpose is one which has a narrow sharp band in the middle of the spectrum, whose

[4] (a) Ref. 2 d. (b) White and Acree, THIS JOURNAL, **40**, 1092 (1918). (c) Tingle, *J. Soc. Chem. Ind.*, **37**, 117(t) (1918). (d) Baker and Davidson, *Phot. J.*, **62**, 375 (1922). (e) Holmes, THIS JOURNAL, **46**, 208 (1924).

[5] Hildebrand, *Z. Elektrochem.*, **14**, 349 (1908).

[6] Bjerrum, *Samml. Chem. Tech. Vortrage*, **21**, 30 (1914).

color change covers a fairly wide range of hydrogen-ion change, whose band at its maximum is quite intense, and the secondary band, which appears on the reduction of the primary band, is far enough removed from the latter so that it does not affect the determination of the height of the primary band. If possible, the secondary band should also be in the visible portion of the spectrum so that further continuous observations can be made on the indicator. An indicator satisfying all of these conditions might not necessarily be an ideal indicator, as it must have chemical properties which will cause it to resist certain reagents.

The indicator which comes nearest to satisfying this requirement is probably thymol blue, although the range that it covers is rather uncommon. The intermediate range within which thymol blue does not give any change can be covered by a mixed indicator of methyl red and bromothymol blue. This gives two indicator solutions capable of covering the entire range from 1.0 to 10.0 *P*H. The curves formed by these two solutions do not overlap to any great extent, and since the accuracy decreases as the maximum or minimum height of the curves is approached, other indicators were studied which covered these ranges, making it possible to obtain more accurate data at these values.

On account of their brilliancy, permanence, the shapes of their absorption bands, and the positions of the bands in the spectrum, the Clark and Lubs indicators[7] seem quite superior to almost all of the common indicators, with the possible exception of phenolphthalein which is a phthalein dye like the Clark indicators. Methyl red, which is not a phthalein dye, is not as satisfactory as the other indicators of this series, but must be used as it covers a range that is not covered by any other of these indicators.[8]

Apparatus

The spectrophotometer was a Keuffel and Esser Model C direct reading color analyzer, with a lamp housing containing the standard magnesium carbonate block holders in a direct line with the solution tubes, rotating sector discs and constant deviation spectroscope. The light source consisted of two 400-watt projection Mazda lamps. The tubes supplied with the instrument proved unsatisfactory for the purpose of this research, as they were made of copper alloy and were affected by the alkali or acid in the solutions to be tested. A much simpler tube was used in this work which gave quite satisfactory results. It was so constructed that the only surface in contact with the solution was glass and it was possible to empty, wash and refill the tube in a very short time. For the experiments described in this paper, tubes 5 cm. in length were used. The

[7] Ref. 2 d, p. 74.

[8] Recently some new sulfonephthalein indicators have been prepared, among which is bromocresol green, which almost perfectly covers the hydrogen-ion concentration of methyl red. (a) B. Cohen, *Public Health Repts.*, **38**, 199 (1923).

rubber caps on the tubes have a decided advantage over metal in that they prevent to a large degree the warming up of the solutions due to conduction of heat.

Inasmuch as the curves which were being studied were sharp and pronounced, it was found much more satisfactory to set the transmission for

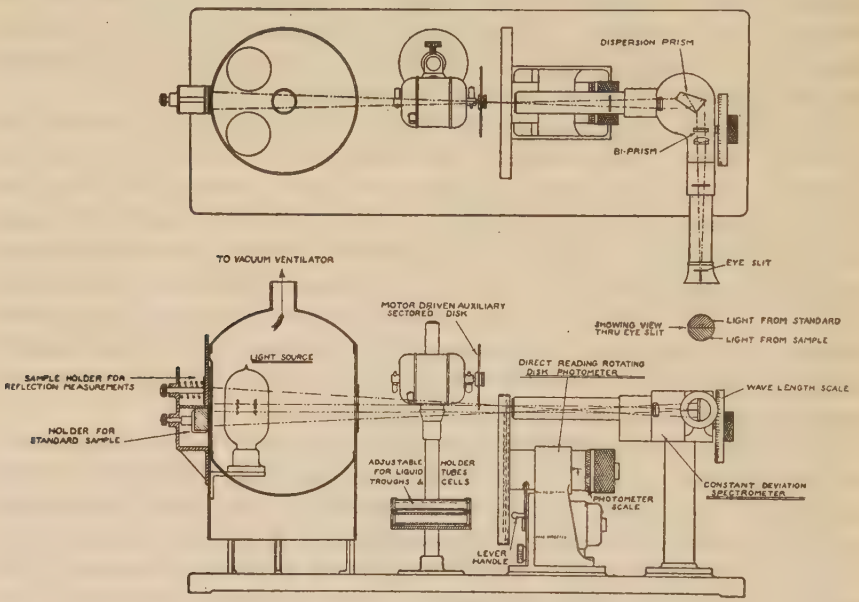

Fig. 1.—Optical system.

certain definite values and adjust the wave length until the two halves of the field matched, rather than set the wave length at a definite value and adjust the transmission. Values for the transmission settings were so chosen as to give direct values for the "—log." of the transmittancy or the extinction coefficient, at intervals of 0.10 from 0.00 to 2.00.[9] In this way twenty different settings were made of the transmission discs and the position of the band noted for both sides of it throughout this series of settings, or as far as the band extended. In the case of a substance which gave a broad flat band this method was not as satisfactory or did not give as many readings as one which required the setting of the wave length at definite intervals and the adjusting of the transmittancy to obtain the necessary data.

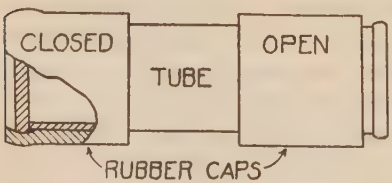

Fig. 2.—Absorption cell.

[9] Gibson and others, *Bur. Standards* (*Sci. Paper*, **440**) **18**, 124 (1922).

The readings were all made within 15 minutes of the time that the indicator was introduced into the solution and in most of the cases observed, the curves were completed within ten minutes. Data for the entire curve were obtained for each solution and the points obtained recorded directly on special graph paper so that any discrepancy caused by misreading a number on either of the two discs could be rectified before the solution was discarded. In practice, however, for the determination of the hydrogen-ion concentration in solutions, it would not be necessary to determine the entire curve but merely the peak of the curve, so that the determination could be done in a much shorter time.

Experimental Part

The buffer solutions used with the indicator solutions to give definite values of hydrogen-ion concentration were for the most part made up according to the Clark and McIlvain buffer standards.[10] By this means buffer solutions were obtained covering a range of 1 to 10 P_H at intervals of 0.2 P_H and in some cases two different buffers were obtained which covered the same values, so that a check reading could be made on them.

The following strengths of indicator solutions[11] were made up after first determining the maximum height of the band produced when 1 cc. of the initial indicator solution, made according to the directions of Clark and Lubs, was added to 50 cc. of solvent, and then this indicator solution was diluted to a final strength which would give an absorption band that approached an extinction coefficient of 2.00 at its maximum.

TABLE I

STRENGTHS OF INDICATOR SOLUTIONS

Indicator	Initial g. per 100 cc.	Final g. per 100 cc.	Ratio of final to initial	P_H range of indicator
Thymol blue	0.04	0.04	1.0	1.2– 3.4
Bromophenol blue	.04	.02	0.5	2.4– 5.6
Methyl red	.02	.015	.75	3.4– 7.0
Bromocresol purple	.04	.032	.8	4.8– 7.6
Neutral red	.02	.0266	1.33	5.6– 8.4
Bromothymol blue	.04	.04	1.0	5.8– 8.4
Phenol red	.02	.0133	0.66	6.2– 9.2
Cresol red	.02	.016	.4	6.8– 9.6
Thymol blue	.04	.032	.8	7.4–10.2
Phenolphthalein	.02	.01	.5	8.0–10.6

Other indicators, such as congo red, methyl orange, benzopurpurin 4B, methyl violet, etc., were tried, but the band was too broad, the secondary band too near the primary, or the indicator so unstable that the change in the height of the band was small or difficult to determine. For the solutions mentioned above, water was used as a solvent except in the cases

[10] Ref. 2 d, pp. 111–116.

[11] Ref. 2 d, p. 80.

of methyl red, phenolphthalein and neutral red. In the first two of these 95% alcohol was used, and in the latter 50% alcohol.

To 50 cc. of the buffer solution of known hydrogen-ion value, 1 cc. of the prepared indicator solution was added, the solution thoroughly shaken and the absorption spectra immediately determined. This process was repeated for each indicator covered by that particular hydrogen-ion value and for all hydrogen-ion values at intervals of 0.2 P_H from 1.2 to 10.0 P_H. From these series of curves, obtained by the determination of the absorption spectra of each of these solutions, another set of curves was derived, by plotting the height of the absorption band in terms of the extinction coefficient, against the hydrogen-ion values for each of these bands. These curves which correspond to dissociation curves[5,6] are similar for all of the indicators tried and afford a more condensed form for comparison of the heights of the bands, and a quicker method for determining the hydrogen-ion concentration of an unknown solution by the spectrophotometric method.

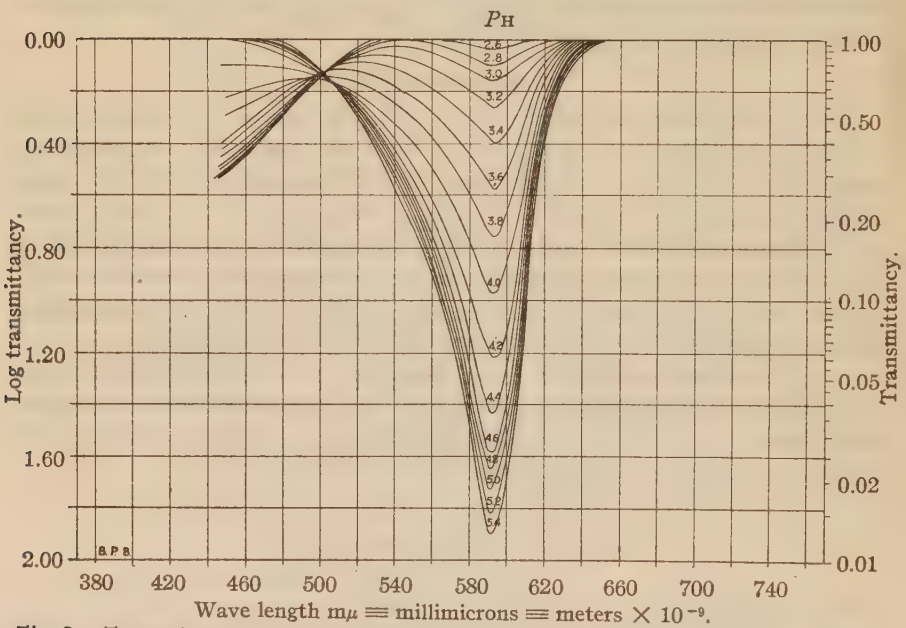

Fig. 3.—Transmittancy curves for bromophenol blue from 2.2 to 5.4 P_H: cell thickness (b) = 5 cm.; concentration (c) = 0.04 g. per 100 cc.

The curves for phenolphthalein were similar to the primary band only of bromophenol blue (there being no secondary band); maximum at 553 mμ, range (8.4 – 10.0 P_H) b = 5 cm.; c = 0.01 g.

In using the condensed graph for this determination, it is not necessary to determine the entire curve of the absorption band, but simply the peak

of the curve. For this reason it is convenient to know the wave length of the absorption bands for the indicators used, the values given being determined from the curves described in this paper.

TABLE II

WAVE LENGTHS OF ABSORPTION BANDS

Indicator	Wave length mμ	Indicator	Wave length mμ
Thymol blue (acid)	544	Cresol red	572
Bromophenol blue	592	Phenol red	558
Methyl red	530	Thymol blue (alk.)	596
Bromocresol purple	591	Neutral red	533
Bromothymol blue	617	Phenolphthalein	553
		Thymolphthalein	598

For work involving a limited range of hydrogen-ion change or where the hydrogen-ion concentration of the solution to be tested is approximately known, the proper indicator may be selected for that range so that the change in the absorption band will be between extinction coefficient values of 0.50 and 1.50, in which range the greatest change in the band takes place and also the greatest accuracy is attained in measuring the height of the band. Where the hydrogen-ion concentration is unknown or where a wide range is to be compared, the best indicators are thymol blue (with a range of 1.0 to 3.5 and 7.5 to 10.0 P_H) and a mixed indicator consisting of methyl red and bromothymol blue, in the same concentrations as in the separate solutions of each of them. This indicator will cover a range of 3.5 to 8.3 P_H although in the middle of this range the accuracy is not as great as might be desired. Values obtained in this part of the curve may be checked by the use of bromocresol purple.

To determine the hydrogen-ion concentration of an unknown solution 2 cc. of the indicator solution is added to 100 cc. of the unknown solution, the mixture shaken thoroughly, and the height of the absorption band in a 5cm. cell determined. The hydrogen-ion value is then determined by comparing the height of this curve against the standard curves given here. In using cells of other lengths than 5 cm. it may be assumed that Beer's law holds for these solutions and the values obtained may, therefore, be reduced to the equivalent of a 5cm. cell. With the help of a color chart[12] or standard samples it is possible to determine the approximate hydrogen-ion concentration and whether the correct indicator has been used. In the case of colored dye solutions the 2 cc. of the indicator solution are added to the 100 cc. of the colored solution and the absorption band determined in the usual manner, except that in place of a colorless solvent in the standard or compensating cell of the spectrophotometer, there will be the dye solution of unknown hydrogen-ion concentration, without the

[12] Ref. 2 d, p. 52.

indicator solution. For extreme accuracy, the standard solution should be diluted with 2 cc. of the original colorless solvent for each 100 cc. so as to compensate for the dilution of the dye solution by the indicator solution.

Discussion of Results

The curves obtained in the investigation of the effect of hydrogen-ion concentration on the absorption spectra of these indicators are of interest from a theoretical as well as a practical point of view. They show clearly that for at least two classes of dyes, namely, phthalein and azo dyes, the

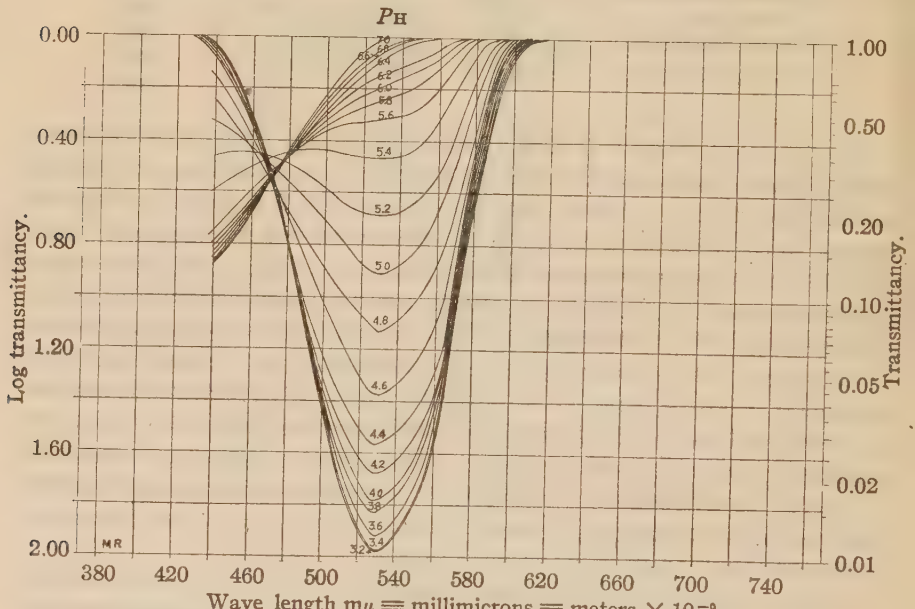

Fig. 4.—Methyl red (3.2 – 5.4 P_H); b = 5 cm.; c = 0.015 g.

The curves for neutral red were similar to those for methyl red; maximum 533 mμ; intersection of curves at 480 mμ; 0.10 transmittancy; range (5.8 – 8.6 P_H) b = 5 cm.; c = 0.0266.

absorption band does not shift in wave length but simply changes in intensity with a change of hydrogen-ion concentration. This rule does not hold for all classes of dyes; for example, the absorption band of methyl violet, a triphenylmethane dye, changes in wave length with only a slight change of intensity, upon a change of hydrogen-ion concentration. This effect is being further investigated and agrees with the data of Holmes[13] and with unpublished observations by Appel and Brode of the United States Bureau of Standards on the fact that the triphenylmethane dyes do not necessarily obey Beer's law and that their color production appears to be of a different type from that of the azo dyes. The curves presented

[13] Holmes, *Ind. Eng. Chem.*, **16**, 35 (1924).

here also show that a secondary band appears on the disappearance of the primary band and that at certain hydrogen-ion concentrations there is an equilibrium between the heights of the two bands.

The existence of absorption bands of definite wave lengths and of an equilibrium between two types of color-producing molecules, is in accordance with recent color theories[14] that a definite configuration and frequency of vibration exists for each color of a certain substance. The way in which the fading of the band takes place fails to confirm theories that intermediate

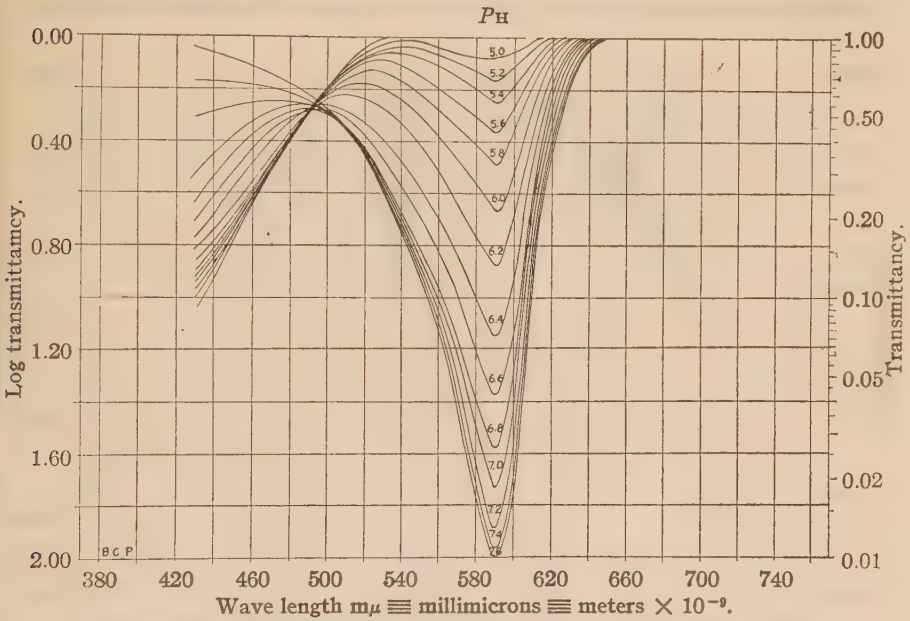

Fig. 5.—Bromocresol purple (4.8 — 7.6 P_H); b = 5 cm.; c = 0.016 g.

The curves for thymol blue (acid) were not completed within the range of Sörensen values studied. They were similar in shape to the bromocresol purple curve but had a maximum at 544 mμ and an intersection of the curves at 485 mμ and 0.30 transmittancy; range (1.2 — 3.4 P_H); b = 5 cm.; c = 0.04 g.

colored products exist between any two principal colored modifications,[15] as the curve retains the same general continuity and does not change on one side of the center of absorption more rapidly than on the other. Another interesting point is that in practically all of the curves studied, there was one point at which all curves of various Sörensen values crossed in changing from one colored form to the other, this point being about midway between the centers of the two bands. It is hoped that it will be possible to study the ultraviolet absorption spectra of these indicators with special

[14] Moir, *J. Chem. Soc.*, **121**, 1555 (1922). Hantzsch, *Ber.*, **48**, 158 (1915). Watson, "Color in Relation to Chemical Constitution," Longmans, **1918**. Ref. 2 d, p. 54.

[15] Moir, *J. Chem. Soc.*, **123**, 2792 (1923), and Ref. 14.

reference to the relation between the structure of the dyes, the number, shape and order of appearance of the various bands and the hydrogen-ion concentrations required to produce or diminish the various bands.

The determination of acidity or alkalinity by spectroscopic means was suggested by Tingle[4c] in which the lateral shifting of the band was measured by a simple spectroscope. The conclusion was drawn that "the absorption bands of colored solutions in most cases, shifted in wave length rather than the substitution of one band for another" with a change of hydrogen-ion concentration. By using a simple spectroscope and a cell

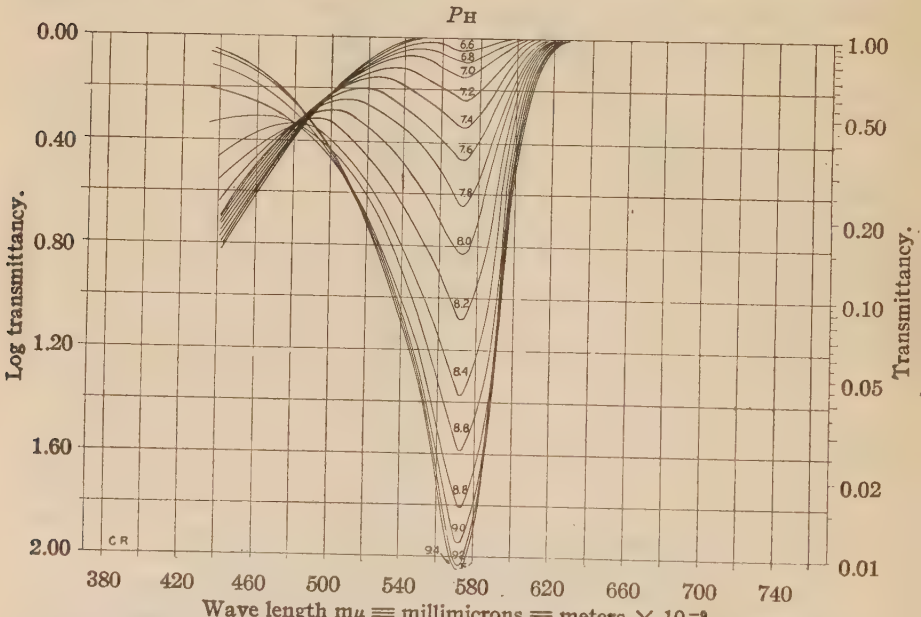

Fig. 6.—Cresol red (6.4 − 9.4 P_H); b = 5 cm.; c = 0.016 g.

The curves for phenol red were similar to those for cresol red; maximum 558 mμ; intersection of curves at 481 mμ; 0.45 transmittancy; range (6.2 − 9.2 P_H); b = 5 cm.; c = 0.0133 g.

of constant thickness, one obtains the same effect as that which results from the following of the curves here presented at one definite extinction coefficient. The apparent effect thus obtained is a lateral shift in the band, due of course to the simultaneous change of the height of the peak. This effect is especially true with azo dyes (Tingle used methyl orange) where the secondary band is near the primary and the bands are quite broad. The same conclusions were reached by Smith and Boord,[16] in regard to the position of the peak of the absorption band of certain azo dyes in solutions of various bases and different strengths of solutions

[16] Smith and Boord, This Journal, 44, 1449 (1922).

Although they used a spectrophotometer they did not measure the peak of the band, but simply the side of the band near the base and from that concluded that the addition of alkali (or acid) caused a "decrease in the frequency of the center of the vibration producing the absorption band," and that the band varied in wave length rather than in intensity. Baker and Davidson[4d] have measured photographically the absorption spectra of a number of the Clark indicators at various hydrogen-ion concentrations and found that the ratio between the two different color components of the indicator is dependent solely on the hydrogen-ion concentration of the

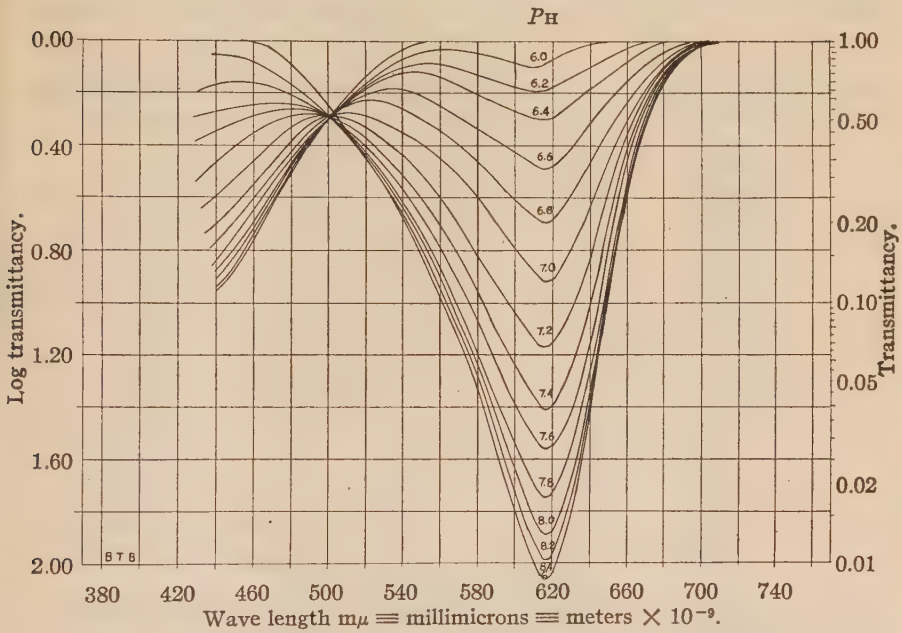

Fig. 7.—Bromothymol blue (5.8 – 8.4 P_H); b = 5 cm.; c = 0.04 g.

The curves for thymol blue (alkaline) were similar to those for bromothymol blue; maximum at 596 mμ; intersection of curves at 500 mμ; 0.47 transmittancy; range (7.4 – 10.0 P_H); b = 5 cm.; c = 0.032 g.

solution and not on the amount of indicator present. Their data also confirm the fact that the absorption bands of these indicators change in intensity rather than in wave length with a change of hydrogen-ion concentration.

It is noticeable that the band after reaching a certain hydrogen-ion value which gives it a maximum height, remains constant at this value over a considerable range of hydrogen-ion concentration and then in certain cases, on further treatment with alkali or acid, as the case may be, it again begins to drop and a different band appears. The shape of the phthalein and sulfonephthalein curves particularly adapts them to use as indicators,

as they are narrow, sharp and show a relatively large change in the position of the absorption-band maximum in relation to the change in the hydrogen-ion concentration of the solution. The azo dyes, on the other hand, have broad curves with a secondary band so near the primary that it adds to the effect of the primary and reduces the amount of possible change in the transmissive index, with a change in the hydrogen-ion value of the solution. The use of methyl red, however, was necessary, due to the fact that in this investigation there were no phthalein dyes available which covered the particular hydrogen-ion range covered by methyl red.[8a]

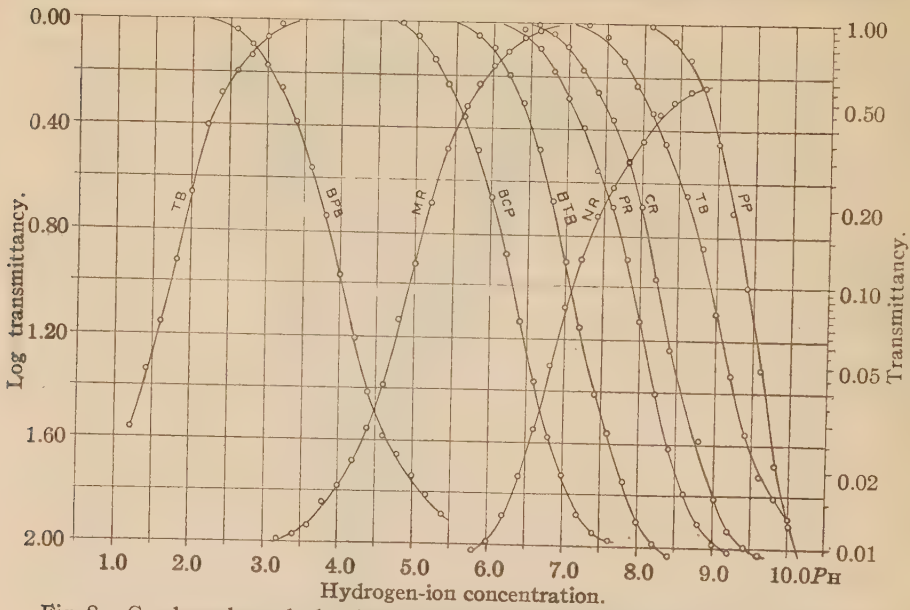

Fig. 8.—Condensed graph showing the relation between the extinction coefficient of the peak of the bands (—log transmittancy) and the hydrogen-ion concentration of the indicator solutions.

The dissociation or ionization constants of the indicators studied may be determined in a manner similar to the method applied to phenolphthalein, methyl orange, etc.,[17,5,6] the constant being taken as the middle point on the condensed curve between the maximum and minimum heights of the band, or approximately on the line representing an extinction coefficient of 1.00. The values obtained agree closely with those obtained by Clark.[18]

Application and Limitation of Method

Unknown solutions were made up from various buffer solutions and the hydrogen-ion concentrations determined both by this method and by the

[17] Prideaux, "Theory and Use of Indicators," Constable, 1917, p. 127.

[18] Ref. 2 d, p. 55.

TABLE III

DISSOCIATION CONSTANTS OF INDICATORS

Indicator	Spectrophotometric value	Clark's value	Indicator	Spectrophotometric value	Clark's value
Thymol blue (acid)	1.75	1.7	Bromothymol blue	7.10	7.0
Bromophenol blue	4.05	4.1	Phenol red	7.90	7.9
Methyl red	4.95	5.1	Cresol red	8.20	8.3
Bromocresol purple	6.30	6.3	Thymol blue (alkaline)	8.90	8.9

electrometric method. The electrometric determinations were made with a palladized electrode in a special type of quartz hydrogen electrode developed by Dr. T. E. Phipps.

TABLE IV

DETERMINATIONS BY THE SPECTROPHOTOMETRIC METHOD, AND ERRORS INVOLVED

Soln. no.	P_H (elec.)	P_H (spectra)	Error	Indicator used
1	1.62	1.59	—0.03	T. B.
2	3.42	3.42	.00	B. P. B.
3	3.44	3.43	− .01	B. P. B.
4	4.40	4.42	+ .02	B. P. B.
4	4.40	4.48	+ .08	M. R.
5	6.60	6.57	− .03	B. C. P.
5	6.60	6.58	− .02	N. R.
5	6.60	6.57	− .03	B. T. B.
6	7.58	7.53	− .05	N. R.
6	7.58	7.59	+ .01	B. T. B.
6	7.58	7.58	.00	P. R.
6	7.58	7.66	+ .08	C. R.
7	7.85	7.92	+ .07	P. R.
7	7.85	7.87	+ .02	C. R.
8	8.19	8.29	+ .10	P. R.
8	8.19	8.29	+ .10	C. R.
9	8.44	8.50	+ .06	P. R.
9	8.44	8.42	− .02	C. R.
10	8.67	8.61	− .06	T. B.
11	8.80	8.76	− .04	C. R.
12	9.20	9.15	− .05	P. P.
12	9.20	9.22	+ .02	T. B.
13	9.39	9.36	− .03	P. P.
13	9.39	9.32	− .07	T. B.
		Av. error	0.042 P_H	
		Mean error	±0.0054 P_H	

The method may be applied somewhat better to cloudy or milky solutions than to colored solutions. Intensely colored solutions cannot be determined by this method, but dye solutions of the strength usually employed in spectrophotometric analysis, where the peak of the band is to be determined, can be used. A suitable concentration for the determination of their absorption bands and one which permits the use of this method is about 0.2 to 0.25 cg. of dye per liter of solution. In using cells of other

thickness this concentration may be varied accordingly. The error involved in the determination of the hydrogen-ion concentration of a colored solution is somewhat greater than the above, due to the reduction of the intensity of the light transmitted through the cell, especially if the absorption band of the colored substance is near that of the indicator. The error, however, is not as great as that which would probably be incurred in measuring the small amount of indicator solution. In the determination of hydrogen-ion concentration by this method it is suggested that check observations be made on buffer solutions or on other solutions of known

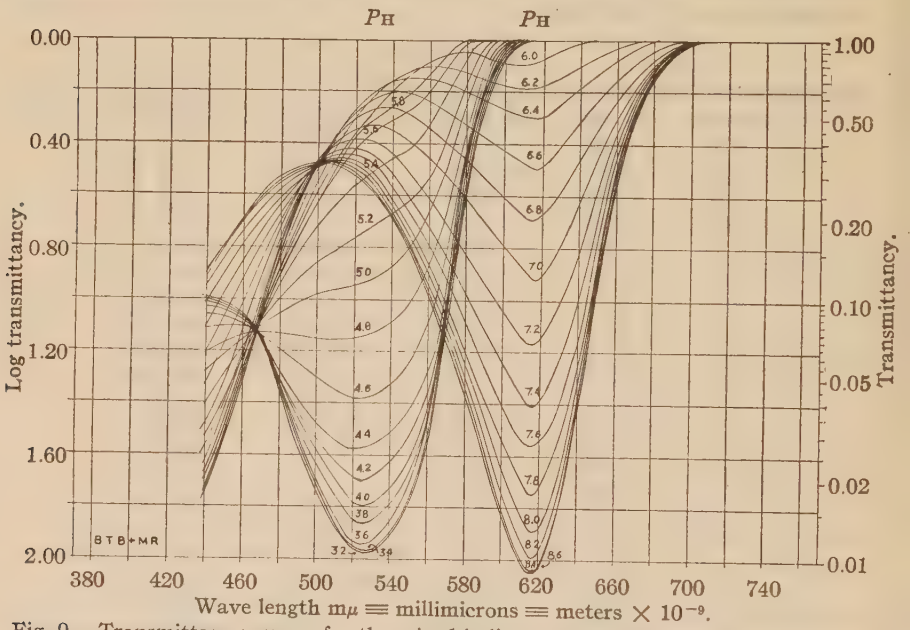

Fig. 9.—Transmittancy curves for the mixed indicator of methyl red and bromothymol blue (3.2 − 8.6 P_H); b = 5 cm.; c of M. R. = 0.015 g.; c of B. T. B. = 0.04 g.

hydrogen-ion concentration, in order to eliminate any possibility of error in the preparation of the indicator solutions or other mechanical errors in the spectrophotometer.

In this experimental work no attempt has been made to correct for any "salt effect." The work of Acree[19] has shown, however, that in the case of buffer solutions of the concentrations of the Clark solutions, the salt effect is small; for example, the correction for a 0.04 N phosphate mixture was 0.02 P_H and this concentration was greater than those of nearly all of the solutions used in these experiments. Inasmuch as this method is

[19] Brightman, Meacham and Acree, *J. Bact.*, **5**, 169 (1920), and other articles by Acree and co-workers in the *Am. Chem. J.*, and THIS JOURNAL.

intended for the determination of the hydrogen-ion concentration in solutions containing only 0.25 cg. or less of dye per liter, it would be permissible to neglect the salt effect, providing the buffer solvent for the dye did not contain a salt concentration greater than that in the Clark buffer standards.

The author wishes to express his appreciation of the suggestions given by Professor Roger Adams of the University of Illinois, and Dr. C. E. Waters and Dr. W. D. Appel of the United States Bureau of Standards, during the progress of this work.

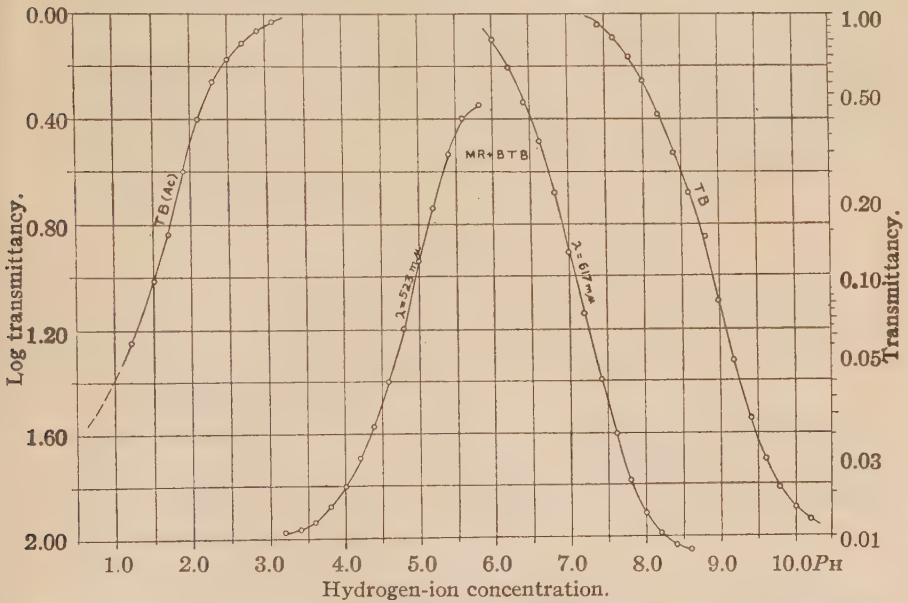

Fig. 10.—Condensed graph showing the relation between the extinction coefficient of the peak of the bands and the hydrogen-ion concentration of the indicator solutions of thymol blue and methyl red-bromothymol blue; b = 5 cm.; c of T. B. = 0.0266; c of M. R. = 0.015; c of B. T. B. = 0.04. Data on M. R. taken at 523 mμ.

Summary

A new method has been proposed for the rapid determination of the hydrogen-ion concentration of dye solutions and other solutions which are being studied spectrophotometrically.

Data are included, showing the effect of the change of hydrogen-ion concentration on a number of common indicators and that the height of the absorption band of these indicators is, within certain limits, a function of the hydrogen-ion concentration of the solution.

From the curves obtained it has been shown that on the change of the hydrogen-ion concentration the center of the absorption band (the peak) does not change in wave length, but rather in intensity.

A secondary band is in equilibrium with the primary band and on the decrease of one of the bands the other increases in height.

The dissociation constant for the indicators studied was determined by a photometric method.

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